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PHOTO-SPECTOGRAPHY OF COLORED FLUIDS

By MOSES C. WHITE, M. D., New Haven, Conn.

WITH ONE PLATE

Every person with a moderate knowledge of mathematical optics is more or less familiar with what are known as the Fraunhofer lines in the solar spectrum, and they know too that incandescent vapors of different metals give characteristic bright lines in the spectra of flames in which the various metallic and non-metallic substances are volatilized. It is not so generally known that many fluids, both colored and colorless, give characteristic dark lines when light passed through them is transmitted through the spectroscope. It is thus that the purity of olive oil may be determined by the spectroscope, which shows dark bands quite different from those produced by any other oil, intercepting the light admitted to the spectroscope. The examination of blood stains in medico-legal cases calls for some color test to distinguish blood from other colored fluids. It is well known that carmine, madder, alkanet, cineraria, permanganate of potash, wine, and many other fluids often look so much like blood as to give much trouble to distinguish them.

The peculiarity of the spectrum as modified by the presence of blood has been ably described by many writers, and yet our books give only diagrams.

Chemists give attention to the spectra of gases and astronomers are spending hundreds of thousands of dollars photographing the light of the stars, and still more, photographing the corona of the sun in total eclipse of that orbit, hoping to learn more of the quality and condition of the matter composing that wonderful luminary. But the character of the lines shown in the spectra of fluids is so different from the lines shown by incandescent gases, that I have thought it might be both interesting and useful to show by photography the absorption bands of blood and other colored fluids.

In entering upon this work we are met at once by the great difficulty of photographing red light. The portrait photographer knows too well the red photographs, as blood and blue and violet appear in the photograph as almost pure white. Most colored fluids give their characteristic absorption bands in or near the red end of the spectrum, and it is well known that the so-called orthochromatic plates used by the modern photographer, while highly sensitive to blue and yellow, are almost wholly insensitive to ruby red, as it is ruby light and that only which is allowed in the dark room while developing modern dry plates.

Plates then that are sensitive to red must be developed mostly in total darkness, and that is what astronomers do in preparing photographs of the sun and stars.

Pure olive oil (Gallipole) in a tube $\frac{5}{8}$ to $\frac{3}{4}$ inch in diameter presents a dark shadow, or cutting out of the blue and violet ray with a fine almost indistinct line in the green and a strong dark band in the red.

Refined cotton-seed oil presents the same appearance as regards the blue and violet only, but the blue and the red are continuous. If cotton-seed oil is mixed with the olive oil, there is no change in the blue and violet rays, but an almost entire fading out of the delicate line in the green and considerable diminution of the dark band in the red.

With 50 per cent of cotton-seed oil the loss in intensity is considerable. With 25 per cent the variation is discernible.*

To photograph the spectrum of colored fluids, specially prepared plates are required. To sensitize the plates for the red end of the spectrum cyanine is used according to the following formula which comes to us from Germany. These plates will not retain their sensitiveness to red more than four or five days. The cyanine plates require long exposure, five or ten times as long as the same plates if not bathed in cyanine; hence fast plates are selected for this work.

Take a solution of cyanine (1 to 1000) in absolute alcohol, 6 ccm.

Codeia solution in absolute alcohol (1 to 1000), 34 ccm.

Aniline oil, chemically pure, 5 drops.

Distilled water, 960 ccm.

In this mixture bathe the plates two minutes.

Then rinse the plates one minute in alcohol, 34 ccm.;

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*Chemical News, quoted in Scientific American, August 28, 1880, No. 243, p. 3874; also Olive Oil, Scientific American Supplement, June 28, 1884.

distilled water, 966 ccm. Wipe the back of the plates with filter paper and dry rapidly in the dark; using chloride of calcium to hasten the drying. If successfully prepared, these plates are sensitive to all the colors of the spectrum, from the ultra violet to the extreme red.

Figure S (Pl. XX) shows the entire length of the spectrum photographed as white of nearly uniform intensity. The solar spectrum is shown with the Fraunhofer lines sharply defined. In contrast with the Fraunhofer lines we see the absorption bands of blood (Fig. B, Pl. XX) wider, less sharply defined, and increasing in breadth as the solution is more dense. The line nearest the red, close to the line D of the solar spectrum, is more dense and more sharply defined than the second line (in the orange) which is broader and paler. Then we see the whole of the space belonging to the blue and violet is cut off by one broad absorption band produced by the blood.

Didymium sulphate (the nitrate gives the same bands), a solution in water with a slightly pinkish hue, gives two absorption bands—the first placed close to the D line in the solar spectrum, which is seen in the photograph (Fig. D, Pl. XX) as a brown shadow close to the left or red side of the first didymium line. The second didymium line, narrower and sharper than the first, lies about two-thirds of the distance from D toward E of the solar spectrum. In the blue and violet portions of the spectra of blood and didymium are seen lines produced by the carbons of the electric arc light used in producing the photographs.

Figure P (Pl. XX) shows a series of beautiful lines of varying size and intensity in the spectrum of a solution of permanganate of potash. This colored fluid produces three heavy dark absorption bands in the green and a medium band in the orange and a *very fine* line in the yellow.

It will be seen at once that many colored fluids are thus readily distinguished by the spectroscope.

L. MOLOSSEZE ON SPECTRUM OF PICROCARMINATE OF AMMONIA.*

We have long known the double absorption bands which are given by suitable solutions of alkaline carminates. I learned also from Ranvier that the picrocarminate of ammonia shows these two bands. But I did not believe that the spectra of picrocarminate at different degrees of concentration had been sufficiently studied, or that the resemblances and differences between blood and picrocarminate in solutions had been sufficiently described.

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* Archives de Physiologie Normale et Pathologique, Paris, 1877; 23, IV, pp 40-43. Translated by M. C. White, February 29, 1884.

When one examines with the spectroscope solutions of picrocarminate sufficiently concentrated, the *red* and the *orange* rays are alone transmitted. All that part of the spectrum beyond the sodium line, D, is obscured. The violet end of the spectrum is especially dark. In more dilute solutions the part previously dark is cleared up for a little distance from the line D and permits the green rays to pass. As we add still more water to the solution the dark part is cleared up still further, permitting the bluish-green (greenish-blue) to pass. There thus results to the right of D two absorption bands, the first, or the one nearest to D, narrower, while the second is the wider of the two.

Continuing to dilute the picrocarminate the two absorption bands diminish a little in extent and become paler, the first more than the second; at the same time the right or violet end of the spectrum clears up more and more. At last the absorption bands entirely disappear, the second band being the last to disappear. If we compare this series of spectra with those given by haemoglobin in similar conditions, one is struck by the great similarity in concentrated solutions either of haemoglobin or picrocarminate, the red rays only being transmitted. In dilute solutions we find to the right of the sodium line two absorption bands, the first narrow, the second wider, while the right or violet end of the spectrum remains more or less obscure. There are, however, a certain number of differences between haemoglobin and picrocarminate. In the spectrum of picrocarminate the part which first clears up when the solution is diluted little by little corresponds to the clear space which separates the two absorption bands the one from the other; the clear space which we find to the right of the two bands only appears later. In other words, the first absorption band is first separated from the dark part; the second band is separated later. In the spectra of haemoglobin, on the contrary, the part which first clears up is that which is to the right of both bands of absorption, while the bands themselves are only separated when the solution becomes more dilute. The absorption bands of picrocarminate are a little more distant from the sodium line and a little more distant from each other than that of haemoglobin. The clear space which separates the bands of picrocarminate corresponds to the second band of haemoglobin. When we continue to dilute, the solutions of picrocarminate grow pale more rapidly and it is the first band (the one nearest to the sodium line) which disappears first. The bands of haemoglobin remain longer, clear and distinct and the second band is the first to disappear. If one does not fully understand the phenomena which solutions of picrocarminate present he might say that the spectra of haemoglobin and picrocarminate are but little different from each other. The spectrum of picrocarminate is explained by that of carmine and by that of picric acid. The two absorption bands of picrocarminate appear and disappear in the same way as those of carmine. Their positions and intensities are the same. But in the spectrum of carmine the extreme right becomes clear rapidly when the solution is diluted, while it remains dark much longer in the spectrum of picrocarminate.

This obscurity is due to the presence of picric acid. The spectrum of this coloring matter is dark at the right (at the violet end) and becomes clear very slowly. The spectrum of picrocarminate is thus a true combination between the spectrum of carmine and that of picric acid.

NOTE.—At the New York meeting, when Dr. White read this paper, he was, despite advancing years, one of the most active and interested members present, participating in all the discussions with keen enjoyment. He did not have an opportunity to correct the proofs of this article before his last illness had come upon him. Consequently the reader will find no doubt that there are minor errors which have escaped the editor's notice, but which would have been rectified by the author.

EXPLANATION OF PLATE

All figures after photographs by M. C. White.

Plate XX

B. Spectrum of Blood.
D. Spectrum of Didymium Sulphate.
C. Spectrum of Picrocarminate.
P. Spectrum of Permanganate of Potash.
S. Solar Spectrum with Fraunhofer Lines.

PLATE XX